

PATENT SPECIFICATION

1,032,033



Inventor: GEORGE ARTHUR POPE.

1,032,033

Date of filing Complete Specification: May 24, 1963.

Application Date: June 14, 1962.

No. 22817/62

Complete Specification Published: June 8, 1966.

© Crown Copyright 1966.

Index at Acceptance:—B1 E4; C3 B (1D4A, 1D4B, 1D6, 1N2A, 1N2B, 1N4J, 1N7, 1N8A, 1N8B, 1N8X, 1N9X, 1N13X, 1N16A); C3 R (27K2F, 27K5F, 27K7F).

Int. Cl.:—B 01 j // C08g.

COMPLETE SPECIFICATION

NO DRAWINGS

Improvements in and relating to Catalysts

WE, DUNLOP RUBBER COMPANY LIMITED, a British Company of 1 Albany Street, London, N.W.1., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to catalysts for use in the polymerization of organic compounds and to a method of polymerization employing such catalysts.

According to the present invention, a method for the manufacture of a heterogeneous polymerization catalyst comprises reacting an alkyl aluminium compound with a chelating agent and water, and adding to the mixture so formed a further quantity of the alkyl aluminium compound or of a different alkyl aluminium compound.

The invention also includes a method for the polymerization of an organic epoxide which comprises contacting at least one organic epoxide with a catalyst prepared according to the method specified in the immediately-preceding paragraph.

The method of producing a catalyst according to the present invention is usually carried out in the presence of an organic solvent, for instance an aliphatic, cycloaliphatic or aromatic hydrocarbon. Suitable organic solvents are cyclohexane, benzene, and toluene. The use of catalysts prepared as aforesaid enables polymeric epoxides to be obtained consisting at least in part of stereoregulated polymer materials. The use of the catalyst enables a higher yield of a polymeric material to be obtained than hitherto possible.

Any alkyl aluminium compound can be used to prepare the catalysts of the present invention and examples of such compounds are the trialkyl aluminium compounds,

[Price 4s. 6d.]

tricycloalkyl aluminium compounds, dialkyl aluminium hydrides, monoalkyl aluminium dihydrides, dialkyl aluminium halides, monoalkyl aluminium dihalides, dialkyl aluminium alkoxides, monoalkyl aluminium dialkoxides, and complexes of these compounds, for example alkali metal aluminium tetraalkyls such as lithium aluminium tetraalkyls. Preferably, the alkyl aluminium compound is a trialkyl aluminium such as triethyl aluminium, but other compounds in which the alkyl group contains up to 8 carbon atoms can equally well be used.

Examples of the chelating agents which can be reacted with the alkyl aluminium compound are diketones such as acetyl acetone, trifluoroacetyl acetone, dibenzoylmethane; ketoacids such as acetoacetic acid; ketoesters such as ethyl acetoacetate; ketoaldehydes such as formyl acetone; hydroxyketones such as hydroxy ethyl methyl ketone, hydroxy acetone, ortho-hydroxy acetophenone; hydroxyaldehydes such as salicyl aldehyde; hydroxyesters such as ethyl glycolate, 2-hydroxyethyl acetate; dicarboxylic acids and their esters such as oxalic acid, malonic acid, monoesters of oxalic acid; dialcohols and alkoxy acids. Other chelating agents containing two or more chelating functions may also be used and examples of these are 2,5-dihydroxy-parabenzquinone, and bis(1,3-diketones).

The amount of chelating agent that is reacted with the alkyl aluminium compound used to form the reaction product is generally from 0.1 to 2 moles per mole of alkyl aluminium compound, but preferably is from 0.6 to 1.3 moles per mole of alkyl aluminium compound. The amount of water that is reacted with the alkyl aluminium compound used to form the reaction product, in the presence of the chelating

agent, is usually from 0.1 to 2.5 moles per mole of alkyl aluminium compound, but preferably is from 1.5 to 2.5 moles per mole of alkyl aluminium compound.

5 The reaction between the alkyl aluminium compound and the chelating agent and the water is usually carried out in the presence of an organic solvent, as already stated, and at the completion of this reaction, which is
10 usually effected at room temperature, a further quantity of the same or a different alkyl aluminium compound is added to the mixture. Conveniently, the amount of
15 additional alkyl aluminium compound which is added can be the same as the amount initially reacted with the water and the chelating agent, but can be different if desired. A particularly useful catalyst is
20 obtained when the molar ratio of the alkyl aluminium compound to the chelating agent and the water is 1:1:2 and with a further equal amount of alkyl aluminium com-
25 pound added to the mixture at the completion of the reaction. The catalyst is a two-part catalyst consisting of a solid material and a supernatant liquid. If the
30 liquid portion of the catalyst is used alone as a catalyst then a polymer or copolymer is obtained in a high yield but containing a small proportion of stereoregulated
35 material, whereas if the solid portion is used alone as a catalyst then a polymer or copolymer is obtained in a lower yield in the same time but containing a much higher
40 proportion of stereoregulated material. The use of the catalyst according to the present invention, consisting of the liquid portion and the solid portion together enables a
45 polymer or copolymer to be obtained in high yield in an economical time and having a higher proportion of the stereoregulated fraction than when the liquid portion is used alone.

The catalysts of the present invention are
45 particularly useful for the polymerization of organic epoxides or for the formation of copolymers of these epoxides with one or more copolymerizable monomers. Examples
50 of epoxides that may be polymerized, according to the present invention, are the alkylene oxides such as ethylene oxide, propylene oxide, butene oxides, isobutylene
55 epoxide, substituted alkylene oxides such as epichlorohydrin, cycloaliphatic oxides such as cyclohexene oxides, vinyl cyclohexene epoxides, epoxy ethers such as alkyl glycidyl
60 ethers, and other epoxides such as styrene oxide, alpha-methyl styrene oxide and butadiene mono- and dioxides.

65 The method of the invention employing the catalyst is particularly useful for the polymerization of propylene oxide and for the preparation of copolymers thereof with such compounds as allyl glycidyl ether. Homopolymers of propylene oxide have

been prepared by the method of the invention containing from 24 to 30 per cent of crystalline material. The proportion of the crystalline material or the stereoregulated polymer is calculated by measuring the
70 amount of polymer that precipitates from a solution of 1 gramme of the polymer in 100 mls of acetone at 0°C.

The proportion of crystalline material, or stereoregulated polymer, obtained depends
75 on the polymerization temperature and the lower this temperature the higher the proportion. However, lowering the temperature also results in a decrease in the speed of the polymerization reaction and hence a
80 decrease in the yield of polymer or copolymer obtained in a given time. For this reason, it is convenient to carry out the polymerization at room temperature. For
85 example, the copolymer of propylene oxide and allyl glycidyl ether produced after 16 hours at room temperature was obtained in 100 per cent yield and contained 14 to 15 per cent of crystalline material, whereas the
90 copolymer produced after 16 hours at 5°C. was obtained in 60 per cent yield and contained 35 to 40 per cent of crystalline material.

The polymerization is usually carried out in the presence of an organic solvent for
95 the monomer to be polymerized, and suitable solvents are the aromatic hydrocarbon solvents such as benzene and toluene.

The invention is illustrated in the following Examples:— 100

EXAMPLE I

0.2 mole of aluminium triethyl was dispersed in 200 mls of benzene and mixed with 0.2 mole of acetyl acetone and 0.4
105 mole of water. After standing at room temperature for a while a further 0.2 mole of aluminium triethyl was added to the reaction mixture to give a mixture consisting of a yellow-green colloidal-like solid and a
110 pale-yellow solution.

To the heterogeneous catalyst mixture so prepared, was added 198 mls of benzene, 70
115 grammes of propylene oxide, and 4.29 grammes of allyl glycidyl ether. After 16 hours standing a copolymer was obtained and was isolated from the catalyst by washing the benzene solution of the polymer with *n*-hydrochloric acid. The polymer was
120 obtained in a yield of 100 per cent. The copolymer had an intrinsic viscosity of 9.78 and was found to contain 14 to 15 per cent of a stereoregulated fraction.

This Example clearly illustrates that the use of a catalyst prepared in accordance with the invention enables a polymer to be
125 obtained in high yield and having a portion of a stereoregulated polymer.

EXAMPLE II

This Example illustrates the effect on the proportion of stereoregulated copolymer 130

obtained by lowering the temperature of polymerization.

A catalyst mixture was prepared as in Example I but using toluene as solvent instead of benzene.

To the catalyst mixture so obtained was added 198 mls of toluene, and the temperature of the resulting mixture was reduced to 5°C. 70 grammes of propylene oxide and 4.29 grammes of allyl glycidyl ether were then added. The temperature was maintained at 5°C. throughout the polymerization, and after 16 hours the copolymer obtained was isolated as in Example I. The copolymer was obtained in a yield of 60 per cent, had an intrinsic viscosity of 8.70 and was found to contain 35 to 40 per cent of stereoregulated material.

These results show that a much higher yield of stereoregulated material is obtained by reducing the temperature at which the polymerization is carried out.

WHAT WE CLAIM IS:—

1. A method for the manufacture of a heterogeneous polymerization catalyst which comprises reacting an alkyl aluminium compound with a chelating agent and water, and adding to the mixture so formed a further quantity of the alkyl aluminium compound or of a different alkyl aluminium compound.

2. A method according to claim 1 in which the catalyst is formed in the presence of an aliphatic, cycloaliphatic or aromatic hydrocarbon.

3. A method according to claim 1 or 2 in which the amount of the chelating agent reacted with the alkyl aluminium compound is from 0.1 to 2 moles per mole of alkyl aluminium compound.

4. A method according to claim 3 in which the amount of the chelating agent is from 0.6 to 1.3 moles per mole of alkyl aluminium compound.

5. A method according to any one of claims 1 to 4 in which the amount of water reacted with the alkyl aluminium compound in the presence of the chelating agent is from 0.1 to 2.5 moles per mole of alkyl aluminium compound.

6. A method according to claim 5 in which the amount of water is from 1.5 to 2.5 moles per mole of alkyl aluminium compound.

7. A method according to any one of the preceding claims in which the amount of the alkyl aluminium compound added to said mixture is the same as the amount of the alkyl aluminium compound used to

form said mixture.

8. A method according to claim 7 in which the molar ratio of the alkyl aluminium compound used to form said mixture to the chelating agent and to the water is 1:1:2.

9. A method according to any one of the preceding claims in which the alkyl aluminium compound used to form said mixture is a trialkyl aluminium compound in which each alkyl group contains up to 8 carbon atoms.

10. A method according to claim 9 in which the trialkyl aluminium compound is aluminium triethyl.

11. A method according to any one of the preceding claims in which the chelating agent is an organic diketone.

12. A method according to claim 11 in which the organic diketone is acetyl acetone.

13. A method for the polymerization of an organic epoxide which comprises contacting at least one organic epoxide with a heterogeneous polymerization catalyst prepared by reacting an alkyl aluminium compound with a chelating agent and water and adding to the mixture so formed a further amount of the alkyl aluminium compound or of a different alkyl aluminium compound.

14. A method according to claim 13 in which the polymerization reaction is carried out in the presence of an organic solvent for the epoxide or epoxides to be polymerized.

15. A method according to claim 14 in which the organic solvent is an aromatic hydrocarbon.

16. A method according to claim 13, 14 or 15 in which the polymerization is carried out at room temperature.

17. A method according to claim 13 in which the alkyl aluminium compound used to form said mixture is aluminium triethyl.

18. A method according to any one of claims 13 to 17 in which the molar ratio of the alkyl aluminium compound used to form said mixture to the chelating agent and to the water is about 1:1:2, and the amount of the alkyl aluminium compound added to said mixture is the same as the amount of the alkyl aluminium compound used to form said mixture.

19. A method for the polymerization of organic epoxides substantially as described in any one of the foregoing Examples.

20. A polymer or copolymer of an organic epoxide when produced by a method according to any one of claims 13 to 19.

C. H. BOWYER,

Agent for the Applicants.